

Spectroscopic properties of uranium(VI) minerals studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS)

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Summary. We studied the fluorescence properties of 120 uranium minerals in order to provide a data base of potential secondary solids that may form in the flooding process of defunct uranium mines. This data base may provide a link of the fluorescence spectra of the minerals to solution spectra containing so far unknown tertiary and quaternary solution complexes in environmental uranium(VI)-containing waters. In our initial effort to establish the data base, we are focusing on phosphate- and arsenate-containing uranium(VI) minerals. Except for chernikovite $[(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}]$, these minerals show intensive fluorescence emissions bands with a bathochromic shift of up to 18 nm compared to the fluorescence of the uranyl ion in solution.

We found hypsochromic shifts of the fluorescence emission for the uranyl phosphates and bathochromic shifts for the uranyl arsenates. The band spacing of the fluorescence emissions from the $20\,502\text{ cm}^{-1}$ level are comparable to the vibrational frequency available from IR-data. Using these data we estimated the axial U–O bond lengths. The decrease of the vibration frequency from 813 cm^{-1} (saleiite, $[\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10(\text{H}_2\text{O})]$) to 794 cm^{-1} (uranocircite, $[\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12(\text{H}_2\text{O})]$) is related to a slight increase of the U–O bond length by 3 pm.

In both series, the fluorescence lifetime decreases with decreasing crystal water. This is different compared to solution spectra where the lifetime increases as water is displaced from the inner coordination shell.

Comparing the fluorescence data of the mineral troegerite $[\text{H}_2(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8(\text{H}_2\text{O})]$ with the fluorescence spectra of uranyl arsenate solutions, we identified one of the three uranyl arsenate complexes in solution as $\text{HUO}_2(\text{AsO}_4)(\text{aq})$.

Introduction

We studied the fluorescence properties of 120 uranium minerals in order to provide a data base of potential secondary solids that may form in the flooding process of defunct uranium mines. This data base may provide a link of the fluorescence spectra of the minerals to solution spectra containing so far unknown ternary and quaternary solution

complexes in environmental uranium(VI)-containing waters. We recently discovered a new neutral solution species, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ in the waters of a decommissioned uranium mine in Saxony, Germany. We confirmed our finding by several independent laboratory studies, and one of the proofs for the existence of this species was that its fluorescence emission wavelengths were nearly identical to those of the mineral liebigite, $(\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O})$, thus connecting the structure of the mineral to the solution complex [1].

Currently, about 160 uranium minerals are known. The varying anionic component serves as a first distinction of uranium minerals. According to this grouping, the following uranium minerals can be found in nature: phosphates, arsenates, oxides/hydroxides (ianthinite $[\text{UO}_2(\text{OH})_2]$), sulfates (johannite $[\text{Cu}(\text{UO}_2)_2(\text{SO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}]$), carbonates (liebigite $[\text{Ca}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}]$), silicates (uranophane $[\text{CaH}_2[\text{UO}_2/\text{SiO}_4]_2 \cdot 5\text{H}_2\text{O}]$), vanadates (carnotite $[\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}]$), molybdates (cousinitite $[\text{Mg}(\text{UO}_2)_2(\text{MoO}_4)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}]$), and selenates (haynesite $[(\text{UO}_2)_3(\text{OH})_2(\text{SeO}_3)_2 \cdot 5\text{H}_2\text{O}]$). Not all of these uranium minerals show fluorescence properties. Although many of these minerals possess fluorescence properties, only very general information on their fluorescence properties is provided with their systematic description in the literature [2–4]. Detailed spectral information are not available at all, or at best they are very incomplete [5]. Furthermore, many uranium minerals are often found only in very small quantities which prohibits destructive analytical techniques to determine their exact chemical composition.

Because it is impossible to describe here the fluorescence properties of all measured uranium minerals, we selected the uranium minerals containing phosphates and arsenates which are the most common inorganic anions in flood waters of the decommissioned uranium mines in Germany.

Further more, we studied the phosphate and arsenate uranium minerals that differ only in the alkaline earth metal. For example, three different uranyl phosphates are known, saleiite $[\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10(\text{H}_2\text{O})]$, autunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10(\text{H}_2\text{O})]$ and uranocircite $[\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12(\text{H}_2\text{O})]$. By using such mineral series, we studied the influence of the alkaline earth metal on the uranyl(VI) fluorescence.

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We also studied the influence of the crystal water on the fluorescence properties. Minerals that differ only in the number of crystal water are identified by adding the prefix “meta-” to the minerals’ name. Five mineral pairs are known for the alkaline earth uranyl- phosphates and arsenates. We report, as examples, on our studies of the mineral pairs autunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10(\text{H}_2\text{O})]$ – metaautunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})]$ and uranospinite $[\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 10(\text{H}_2\text{O})]$ – metauranospinite $[\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8(\text{H}_2\text{O})]$.

Experimental

The time-resolved laser-induced fluorescence spectra were recorded with the experimental setup described in [6]. During the measurement the samples were held at $19 \pm 1^\circ \text{C}$ and at a relative humidity of $54 \pm 2\%$. A conventional cuvette housing (Acton Research, model SC447) was used with the cuvette holder removed. The minerals were mounted with an adhesive paste on a pivoted table, which allowed the remove of the minerals without damage.

The fluorescence of the minerals was excited by laser pulses at 266 nm. The laser has a repetition rate of 10 Hz and the pulse duration is in the range of 10 ns. To avoid any damage of the minerals, the average applied laser power was set to 500 μJ per pulse and measured with an optical power meter (Newport, Model 1835C).

The fluorescence signal was measured perpendicularly to the excitation laser beam and focussed to the input of a fiber optic cable. The input of this fiber optic cable was placed inside the cuvette housing. The output of the fiber optics was coupled to the entrance slit of a 500 mm spectrograph (M1236, EG&G/Acton Research). The fluorescence signal was measured with a gated intensified diode array (M1492, EG&G). The gate width was set to 1 μs and the fluorescence

was recorded after a delay time ranging from 10 ns to up to 50 μs . For every delay time, the fluorescence signal was averaged by sampling five single spectra over 100 laser shots. The resulting fluorescence spectra were normalized for comparison. GRAMS386 (Galactic Ind. Corp., USA), Origin 5.0 (Microcal Software Inc., USA) and PeakFit 4.0 (AISN Software Inc., USA) were used to process the spectral data.

Results and discussion

All minerals studied are the property of the Minerals Collection of the Technical University Mining Academy, Freiberg, Germany, which preempted the use of any destructive analytical techniques. Therefore, our study was restricted to fluorescence spectroscopy, and no further identification of the chemical composition and XRD measurement of the minerals was possible. We were limited to identifying the chemical composition from the mineral’s chemical nomenclature. Table 1 lists all the minerals studied. Because the chemical composition, especially the number of the crystal water molecules, is sometimes not clearly defined in the literature, we followed the suggestions of the mineral formula database given by J. D. McDonald [4]. If minerals were not included in this database, we used the formula given by Roessler [3]. The inventory numbers of the minerals collection are also listed in Table 1 to clearly assign the measured fluorescence spectra to the appropriate mineral.

The mineral chernikovite does not show measurable fluorescence. This may be caused by several facts. Comparing the fluorescence lifetime of the alkaline earth phosphates and arsenates these data are mostly of the same magnitude (Table 2, the data for $\text{UO}_2^{2+}(\text{aq.})$ are enclosed for comparison [7]). Therefore we should expect the same order for the lifetime of chernikovite as found for troegerite (150 ns). Short fluorescence lifetimes normally are associated with

Table 1. Name, chemical composition and origin of the minerals studied.

Name	Chemical composition	Collecting point
	Phosphates	
Chemikovite	$(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6(\text{H}_2\text{O})$	Hagendorf, Oberpfalz, Germany, FG 72753 ^b
Saleeite	$\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10(\text{H}_2\text{O})^a$	Capeterra, Sardinia, Italia FG 69601
Autunite	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10(\text{H}_2\text{O})$	Joehstadt, Ore mountains, Germany, FG 43241
Metaautunite	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$	Fojtov, Czech Republic, FG 70751
Uranocircite	$\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12(\text{H}_2\text{O})$	Bergen, Saxony, Germany, FG21743
Metauranocircite	$\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$	Honey Comb Hills, Utah, USA, FG 55717
Sabugalite	$\text{HAl}(\text{UO}_2)(\text{PO}_4)_4 \cdot 16(\text{H}_2\text{O})^a$	Erkersreuth, Bavaria, Germany, FG 55835
Threadgoldite	$\text{Al}(\text{UO}_2)_2(\text{PO}_4)_2(\text{OH}) \cdot 8(\text{H}_2\text{O})$	Kobokobo, Kivu, Kongo FG 70002
Ranunculite	$\text{HAl}(\text{UO}_2)(\text{PO}_4)(\text{OH})_3 \cdot 4(\text{H}_2\text{O})$	Kobokobo, Kivu, Kongo 75816
Phuralumite	$\text{Al}_2(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_6 \cdot 10(\text{H}_2\text{O})$	Kobokobo, Kivu, Kongo, FG 75815
	Arsenates	
Troegerite	$\text{H}_2(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8(\text{H}_2\text{O})^a$	Schneeberg, Ore mount., Germany, FG 21801
Novacekite	$\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 12(\text{H}_2\text{O})$	Brumado Bahia, Brasilien, FG 61144
Metanovacekite	$\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 6(\text{H}_2\text{O})$	Wittichen, Black Forest, Germany, FG 67382
Uranospinite	$\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 10(\text{H}_2\text{O})$	Uhiguro, Tierge, Tansania, FG 52356
Metauranospinite	$\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8(\text{H}_2\text{O})$	Wolkenstein, Ore mount., Germany, FG 78104
Heinrichite	$\text{Ba}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 11(\text{H}_2\text{O})$	Wittichen, Black Forest, Germany, FG 45538
Metaheinrichite	$\text{Ba}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8(\text{H}_2\text{O})$	Wittichen, Black Forest, Germany, FG 54215

a: chemical composition according to Roessler [1]

b: the number indicates the inventory of the minerals collection of the Technical University Mining Academy Freiberg

Table 2. Fluorescence properties of the studied minerals.

Mineral	fluorescence emission bands/nm						lifetime/ns	band spacing/cm ⁻¹
Phosphates								
Chemikovite							—	
Saleeite	489.0	501.1	522.1	545.7	570.9	600.9	2250 ± 200	813 ± 13
Autunite	488.6	504.0	524.2	548.0	573.9	602.4	5150 ± 275	805 ± 35
Metaautunite	491.3	501.8	522.9	546.9	572.2	591.7	740 ± 100	817 ± 19
Uranocircite	488.1	503.5	523.9	547.0	572.1	599.7	30 600 ± 950	794 ± 18
Metauranocircite	488.9	502.5	523.7	547.4	573.4	602.6	3000 ± 270	820 ± 12
Sabugalite	491.4	506.4	527.7	550.8	575.9	604.8	3130 ± 130	794 ± 3
Threadgoldite	489.7	501.4	522.1	545.6	571.2	601.3	3180 ± 385	812 ± 18
Ranunculite	491.4	501.2	521.9	545.5	570.5	600.3	1930 ± 145	808 ± 19
Phuralumite	496.9	500.6	520.3	542.9	568.7	599.9	31 800 ± 1300	797 ± 39
Arsenates								
Troegerite	485.5	502.2	524.4	547.4	572.7	604.8	150 ± 25	817 ± 23
Novacekite	486.3	502.6	523.1	546.8	572.8	601.7	6700 ± 360	812 ± 29
Metanovaceckite	492.1	504.3	526.7	549.7	575.5	608.2	840 ± 90	817 ± 24
Uranospinite	488.2	502.2	523.6	547.2	573.0	600.7	3460 ± 170	820 ± 6
Metauranospinite	489.9	502.7	526.8	549.2	574.5	604.3	1660 ± 90	828 ± 72
Heinrichite	495.0	505.8	528.4	551.4	577.7	604.6	33 700 ± 2800	820 ± 28
Metaheinrichite	492.4	505.7	527.9	551.4	576.9	606.1	8060 ± 490	813 ± 16
UO ₂ ²⁺ (aq.); pH 1.0; <i>I</i> = 0.1 M	471.3	488.9	510.5	533.9	559.4	585.5	1800 ± 200	859 ± 8

low fluorescence intensities. Unfortunately the used mineral was a very small crystal placed on rock material. Larger mineral crystals were not available, and the used one is unique to the collection.

We measured the minerals saleeite, Mg(UO₂PO₄)₂ · 10H₂O, autunite, Ca(UO₂PO₄)₂ · 10H₂O, and uranocircite, Ba(UO₂PO₄)₂ · 12H₂O in the series of alkaline earth uranyl phosphates. We studied the influence of the changing alkaline earth ion on the fluorescence of the uranyl phosphate group. The data for the main fluorescence emissions are listed in Table 2. Fig. 1 shows the fluorescence spectra of these three minerals. The spectra were normalized to a maximum emission of 100 and constant values were added to show the spectra in one figure. We found shifts of up to 3.3 nm in the fluorescence emission between these minerals. The fluorescence lifetimes in these series are 2.3 μs,

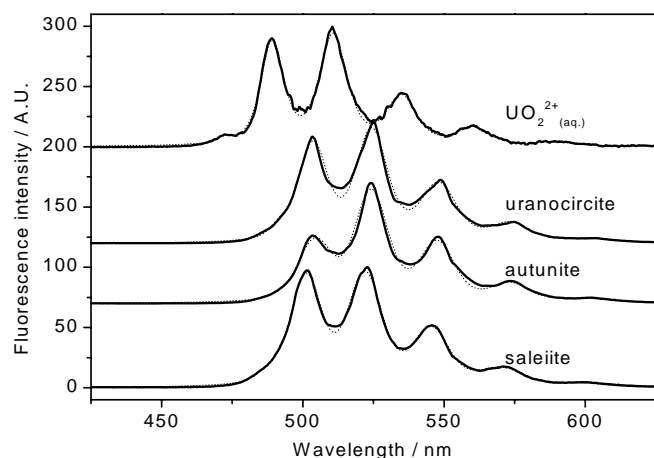


Fig. 1. Fluorescence spectra of alkaline earth uranyl phosphate minerals (dotted lines show the curve fit of the spectra (Lorentzian shape)); the spectrum of UO₂²⁺(aq.) is given for comparison (the band at 532 nm is a residue from the second order detection of the excitation wavelength).

5.2 μs and 30.6 μs, respectively. A discussion of the influence of fluorescence quenchers on the lifetime of the minerals is not possible because no information is available about impurities.

Several spectra show a band at 532 nm. This is related to the detection of the second order of the excitation wavelength generated by the grating in the spectrograph. To remove this spike we deconvoluted the spectra but could not completely eliminate this feature for several cases.

The emission bands were mostly fitted with a Lorentzian shape. In a few cases a Gaussian shape was used. The FWHM (full width at half maximum) of the emission band was between 10 nm and 20 nm. We observed an increase of the FWHM with increasing wavelength of the emission bands.

The vibrational frequency transitions of the ground state can be calculated from the band spacing of the fluorescence emission from the lower radiation emitting level (20 502 cm⁻¹ for the UO₂²⁺) [10]. The higher radiation emitting level does not show this behavior [8]. The symmetrical vibrational frequency of the ground state can be correlated to the U—O axial bond length [9, 10]. The calculated maxima for the fluorescence emissions from the lower excited state were used to estimate the band spacing. The bands are not equally spaced. As the intensity of the emission band from the excited state to the highest level of the ground state vibrational level (~ 600 nm or 16 670 cm⁻¹) is very small, and the determination of the emission maximum for this fluorescence emission is associated with relatively large errors. Therefore, only the maxima of the four other fluorescence emissions for the calculation of the band spacing were used. The calculated band spacings are given in Table 2.

The vibrational levels of the ground state were spaced about 820 cm⁻¹ apart from each other. The IR absorption band in this region is related to the symmetric stretching vibration of the UO₂²⁺ (ν₁-UO₂²⁺, Cejka [11]). The ground state vibrational frequencies for saleeite, autunite and ura-

nocircite are at $813 \pm 13 \text{ cm}^{-1}$, $805 \pm 35 \text{ cm}^{-1}$ and $794 \pm 18 \text{ cm}^{-1}$, respectively. This effect is due to the increase of the atomic radius of the alkaline earth metal bound in the minerals.

Using the empiric relation given by Barlett and Cooney [9]

$$R_{\text{U-Oax}} = 10650 (\nu_1)^{-2/3} + 57.5 \text{ pm} \quad (1)$$

with ν_1 in cm^{-1} , we calculate the axial U–O bond length as $179 \pm 1 \text{ pm}$, $180 \pm 4 \text{ pm}$ and $182 \pm 2 \text{ pm}$, respectively.

If the phosphate group is substituted by arsenate in the alkaline earth uranyl minerals, the following minerals are formed: novaceckite $[\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 12(\text{H}_2\text{O})]$, uranospinite $[\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 10(\text{H}_2\text{O})]$ and heinrichite $[\text{Ba}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 11(\text{H}_2\text{O})]$. The fluorescence emission maxima for these minerals are also listed in Table 2. Fig. 2 shows the overlaid spectra for the alkaline earth uranyl arsenate minerals. Again, a bathochromic shift occurs of up to 5.5 nm from novaceckite to heinrichite. The fluorescence lifetimes are 6.7 μs , 3.46 μs and 33.7 μs for novaceckite, uranospinite and heinrichite, respectively. The change of the fluorescence lifetimes from novaceckite to heinrichite is of the same magnitude as for the phosphate series, but the uranospinite fluorescence shows a shorter lifetime. This may be due to the influence of the crystal water. The mineral uranospinite has less bound water per formula unit than the other two arsenates. Using the same calculation procedure as for the phosphate series, we obtain a band spacing of $813 \pm 27 \text{ cm}^{-1}$, $820 \pm 5 \text{ cm}^{-1}$ and $820 \pm 28 \text{ cm}^{-1}$ for novaceckite, uranospinite and heinrichite, respectively. The calculated axial U–O distances are $180 \pm 3 \text{ pm}$, $179 \pm 1 \text{ pm}$ and $179 \pm 3 \text{ pm}$, respectively. These values are nearly identical to those for the phosphates.

Some minerals differ only in the number of the crystal water molecules per formula unit. In the studied alkaline earth uranyl phosphate and arsenate series, these minerals are metaautunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})]$, metauranocircite $[\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})]$, metanovaceckite $[\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 6(\text{H}_2\text{O})]$, metauranospinite $[\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8(\text{H}_2\text{O})]$ and metaheinrichite

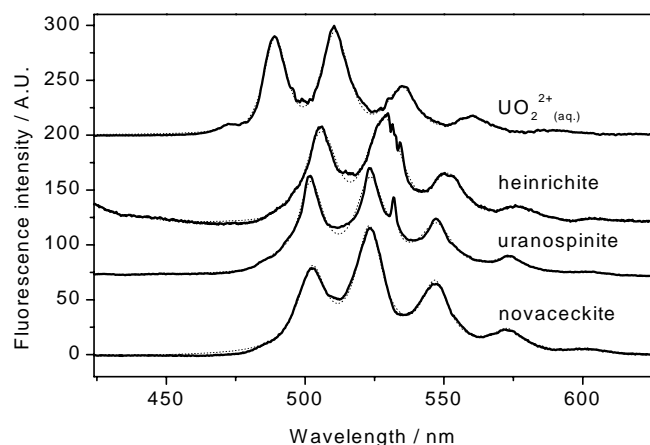


Fig. 2. Fluorescence spectra of alkaline earth uranyl arsenate minerals (dotted lines show the curve fit of the spectra (Lorentzian shape)); the spectrum of $\text{UO}_2^{2+}(\text{aq.})$ is given for comparison (the band at 532 nm is a residue from the second order detection of the excitation wavelength).

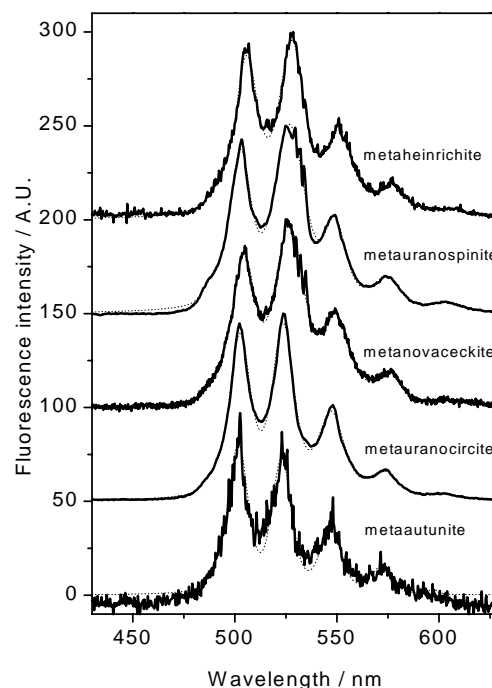


Fig. 3. Fluorescence spectra of alkaline earth uranyl phosphate and arsenate meta minerals (dotted lines show the curve fit of the spectra (Lorentzian shape)).

$[\text{Ba}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8(\text{H}_2\text{O})]$. The data for the fluorescence emission maxima are also listed in Table 2. Fluorescence spectra are shown in Fig. 3. Robbins [5] reports a spectrum of the mineral metaautunite. Because no data are reported on the maxima of the fluorescence emissions, a complete comparison to our spectrum here is not possible. Judging from the peak height distribution and the shape of the fluorescence spectra, the spectrum reported in [5] is rather similar to the autunite spectrum reported here.

Compared to their water-rich analogue most of the meta minerals show a wavelength shift. This shift depends on several chemical changes in the compound. In the case of the calcium minerals (autunite/metaautunite and uranospinite/metauranospinite), the phosphates showed a slightly hypsochromic shift and the arsenates showed a bathochromic shift (Fig. 4). The bathochromic shift is more intensive for the magnesium arsenates. Because the meta magnesium uranyl phosphate mineral was not available, a comparison for the magnesium phosphates is not possible. In the case of the barium minerals (uranocircite/metauranocircite and heinrichite/metaheinrichite) the shift is less intensive and has a tendency for a directional shift change. The emission bands starting at 547 nm of the uranocircite/metauranocircite pair show a bathochromic shift, whereas heinrichite/metaheinrichite shows a slight hypsochromic shift. Because, all these minerals are members of the same crystal lattice group (ditetragonal-dipyramidal), an explanation for this behavior can only be found in the changing of the atomic radii of the alkaline earth metals in combination with the changing anion.

Also the fluorescence lifetimes show an unexpected behavior. In solution chemistry the lifetime of the uranyl ion increases with increasing ionic strength in perchloric media [12]. Therefore an increase of the fluorescence life-

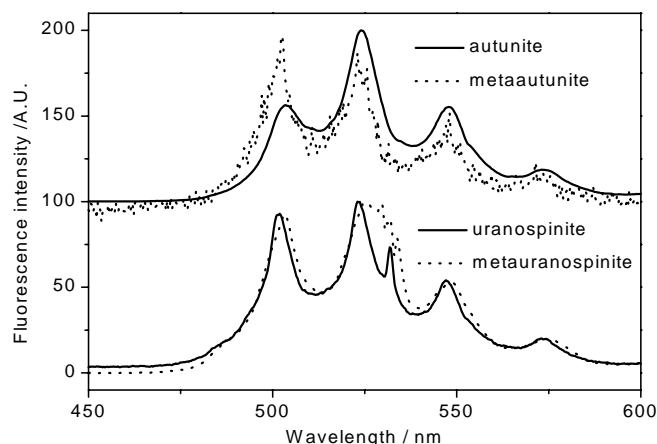


Fig. 4. Comparison of meta uranyl minerals with their water-rich equivalents: novaceckite $[\text{Mg}(\text{UO}_2)_2(\text{AsO}_4) \cdot 12(\text{H}_2\text{O})]$ vs. metanovaceckite $[\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 6(\text{H}_2\text{O})]$ and uranocircite $[\text{Ba}(\text{UO}_2\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}]$ vs. metauranocircite $[\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})]$.

time should occur if a mineral contains less crystal water molecules. We did not find this behavior. We observed for all cases a decrease of the fluorescence lifetime by about one order of magnitude from the water-rich to the less water-containing minerals. Also the fluorescence intensity and the axial U–O bond length, calculated from the band spacing, decreased. Using the data for the longest fluorescence lifetime and the calculated axial U–O bond length, we found a tendency for a linear dependence of the bond length (and the band spacing) on the logarithmic of the fluorescence lifetime (Fig. 5). Using the data from the arsenate series, a much smaller tendency was observed for the plot of the U–O distance as function of the logarithm of the fluorescence lifetime. This may be due to the larger size of the arsenate group which decreases the influence of the alkaline earth metal on the U–O bond length. We are currently verifying this result with data of other uranyl fluorescence spectra.

We also studied the fluorescence properties of the uranyl arsenate mineral troegerite, $\text{H}_2(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8(\text{H}_2\text{O})$. The main fluorescence emission maxima were found to be at 502.2 nm, 524.4 nm, 547.4 nm and 572.7 nm. The deter-

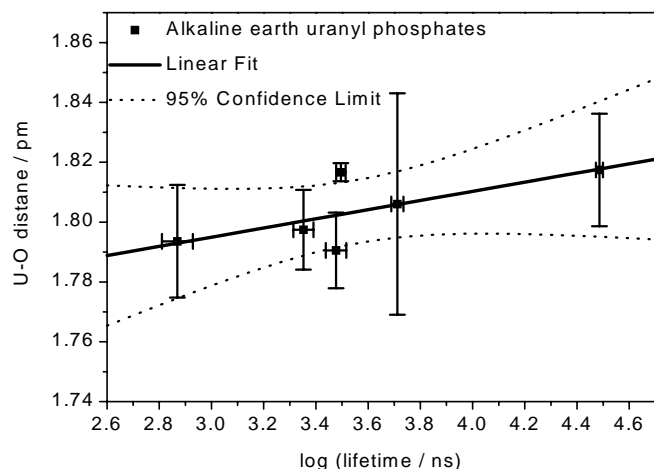


Fig. 5. U–O bond length correlation as a function of the fluorescence lifetime for alkaline earth phosphate minerals (dotted lines are 95% confidence limits).

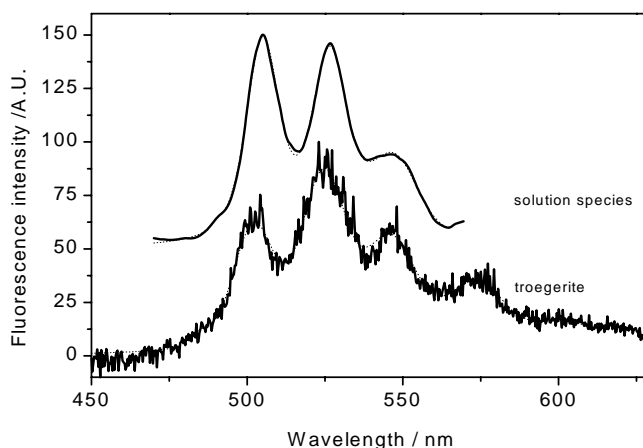


Fig. 6. Comparison between the fluorescence spectra of troegerite and $\text{UO}_2(\text{HAsO}_4)(\text{aq.})$ (dotted lines show the fitted spectra).

mined fluorescence lifetime is $0.15 \pm 0.025 \mu\text{s}$. Fluorescence studies of the $\text{UO}_2^{2+}/\text{H}_3\text{AsO}_4$ system [13] showed that three uranyl arsenate species exist. For one of these species the main fluorescence emission maxima are at 504 nm, 525 nm and 547 nm and the fluorescence lifetime is smaller than $1 \mu\text{s}$. A comparison of the fluorescence spectra of troegerite with the $\text{UO}_2(\text{HAsO}_4)(\text{aq.})$ species is shown in Fig. 6. As the other two uranyl arsenate species in this system have different fluorescence maxima and also much longer fluorescence lifetimes, we assigned this solution species to be $\text{UO}_2(\text{HAsO}_4)(\text{aq.})$.

Conclusions

The fluorescence data of minerals can be used as fingerprints to determine secondary mineral coatings on rock materials, and can support the interpretation of spectra of unknown ternary and quaternary solution species. These data are also useful to identify uranyl(VI) species sorbed on mineral and rock surfaces and on certain bacteria.

By comparing the fluorescence data of several mineral series, we were able to study the influence of secondary metal ions, anions and the bound water molecules on the fluorescence properties of the uranyl group. Information on the axial U–O bond length is derived from the band spacing of the fluorescence emission maxima. The vibrational ground state transition frequency is equal to the IR band of the symmetric stretching vibration ν_1 of the UO_2^{2+} ion. We found an empirical correlation between the vibrational frequency of the ground state and the fluorescence lifetime.

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